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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention The poly imide siloxane of (a) fusibility, (b) epoxy polyoxyalkylene modified polysiloxane, (c) Other epoxy compounds which have an epoxy group, the (d) inorganic bulking agent, and the (e) epoxy curing agent are involved in the heat-resistant adhesives containing by composition ratio specific as a resinous principle.
[0002]The heat-resistant adhesives of this invention can perform lamination at low temperature comparatively, and various metallic foils, such as copper, aluminum, and iron, and charges of a heat-resistant support material, such as a heat-resistant film and an inorganic sheet, for example. The layered product stretched with the aforementioned heat-resistant adhesives, Since adhesive strength with a sufficient adhesives layer is shown and the outstanding heat resistance is moreover shown, For example, if it is used for manufacture of flexible wiring boards, the copper-clad boards for TAB (Tape Automated Bonding), etc., He feels easy about various kinds of high-temperature-processing processes, such as subsequent solder processing, and it can carry out, and the quality of a final product is raised, or each substrate obtained using the heat-resistant adhesives can reduce a defective fraction.
[0003]
[Description of the Prior Art]Conventionally, the flexible wiring board was manufactured by pasting an aromatic polyimide film and copper foil together using adhesives, such as an epoxy resin and urethane resin, in many cases. However, when the flexible wiring board manufactured using publicly known adhesives was put to the elevated temperature at the subsequent solder process, in the adhesives layer, there is a problem of producing a blister and peeling and to raise the heat resistance of adhesives was desired.
[0004]The reserve condensate which imide resin system adhesives are proposed, for example, serves as N,N'-(4,4'-diphenylmethane) bismaleimide from 4,4'-diaminodiphenylmethane as

heat-resistant adhesives is known. However, since this reserve condensate itself is weak, it is not suitable as adhesives for flexible wiring boards.

[0005]As a method of improving said fault, for example in JP,62-232475,A and JP,62-235382,A. An adhesive film (a dry film or a bonding sheet) is formed from the resin composition which mixed the aromatic polyimide obtained from benzophenone tetracarboxylic acid and aromatic diamine, and poly bismaleimide, The method of putting the adhesive film between a heat-resistant film and copper foil, and bonding it by thermo-compression is proposed.

[0006]However, the softening temperature is not less than 180 **, and the aforementioned adhesive film adhesion with a heat-resistant film and copper foil under a high temperature of about about 260-280 **, And it was very difficult to carry out under the high pressure about 30 - 60 kg/cm^2, and to laminate a heat-resistant film and copper foil continuously in such bonding conditions using the sticking-by-pressure roll made of organic resin, and it was a problem in respect of practicality.

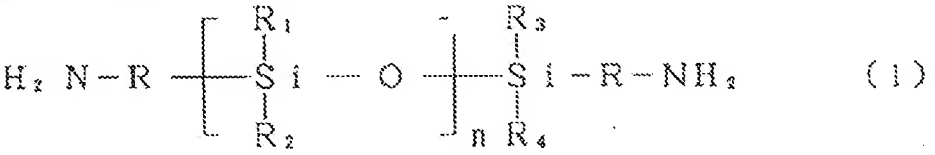
[0007]On the other hand, in order that the resin solution (varnish) which blended the epoxy resin with aromatic polyimide etc. may improve the adhesive property of a heat-resistant coating layer, a patchboard, etc. which consist of said resin curing thing as a constituent for coating of electronic parts, such as a patchboard, many things are proposed, but. As adhesives for pasting up copper foil and the aromatic polyimide film in manufacture of the above copper-clad boards, the publicly known constituent for coating, There is a problem that lamination or the temperature of hardening does not become high, the compatibility of aromatic polyimide and an epoxy resin or the compatibility of aromatic polyimide and a solvent is not low, or the adhesives layer after pasting up and hardening is not flexible, and it cannot actually be used as adhesives.

[0008]

[Problem(s) to be Solved by the Invention]As for the purpose of this invention, the problem in the above-mentioned publicly known adhesives is canceled, It aims at providing the heat-resistant adhesives in which the high adhesive property in the high temperature which can stretch a heat-resistant film and various metallic foils suitably is shown through the process of consisting of spreading of an adhesives solution, desiccation, a lamination of copper foil, and hardening of an adhesives layer.

[0009]This artificer The poly imide siloxane of the fusibility of (a) specification, (b) epoxy polyoxyalkylene conversion polysiloxane, (c) If the resinous principle which combined other epoxy compounds which have an epoxy group, the (d) inorganic bulking agent, and the (e) epoxy curing agent, and was made the specific presentation is used as adhesives, The independent particulate material was formed into matrix resin of the adhesives layer after adhesion / hardening, and it found out presenting the sea island structure which the particle

with a particle diameter of 0.1-5 micrometers distributed uniformly in the adhesives layer, got to know that they were adhesives which can attain said purpose, and resulted in this invention.
[0010]
[Means for Solving the Problem]An aromatic tetracarboxylic acid ingredient to which this invention uses (a) biphenyl tetracarboxylic acid as the main ingredients, and a general formula (1)
[0011]
[Formula 2]



[0012](However, R in a formula shows divalent hydrocarbon and R_2 R_1) R_3 and R_4 show a ** low-grade alkyl group or a phenyl group, n -- 3-60 -- the integer of 5-50 is shown preferably. 10-80 mol of diaminopolysiloxanes % shown. And poly imide siloxane 100 weight section of the fusibility acquired from the diamine component which consists of 20-90 mol of aromatic diamine %, (b) One to epoxy polyoxyalkylene modified polysiloxane 60 weight section, (c) Other 15 to epoxy compound (epoxy resin) 250 weight sections which have an epoxy group, the (d) inorganic bulking agent 0.2 - 20 weight sections, and the (e) epoxy curing agent are related with the heat-resistant adhesives containing as a resinous principle.
[0013]As an aromatic tetracarboxylic acid ingredient which uses as the main ingredients the biphenyl tetracarboxylic acid used in this invention, 3,3',4,4'-biphenyl tetracarboxylic acid, 2,3,3',4'-biphenyl tetracarboxylic acid, or biphenyl tetracarboxylic acid, such as such acid dianhydride, esterification material, etc., -- more than 60 mol % -- especially -- 80-100-mol % -- an aromatic tetracarboxylic acid ingredient to contain is used. Since 2,3,3',4'-biphenyl tetracarboxylic dianhydride is excellent in solubility over an organic polar solvent of said poly imide siloxane, compatibility with an epoxy compound, etc. also especially in these, it is suitable.
[0014]As an aromatic tetracarboxylic acid ingredient which can be used with the biphenyl tetracarboxylic acid used in this invention, For example, 3,3',4,4'-benzophenone tetracarboxylic acid, 3,3',4,4'-diphenyl ether tetracarboxylic acid, Bis(3, 4-dicarboxyphenyl)methane, 2,2-bis (3,4-dicarboxyphenyl)propane, pyromellitic acid, those acid dianhydride, esterification material, etc. can be mentioned suitably. However, if there is too much these amount used, since said poly imide siloxane will serve as poor solubility to an organic polar solvent or compatibility with an epoxy resin will get worse, it is not suitable.
[0015]In 2-6 carbon numbers, R in a formula especially as a diaminopolysiloxane shown by a general formula (1) in this invention 3-5 "two or more methylene groups." Are the divalent

hydrocarbon residue which consists of phenylene groups, and R_1 - R_4 Or a methyl group, It is preferred that they are a low-grade alkyl group or phenyl groups of the carbon numbers 1-5, such as an ethyl group and a propyl group, and it has especially still more preferred n 5-20, and that it is five to about 15 still more preferably. There are too many carbon numbers of R, R_1 - R_4, or if the number of n is too large, reactivity will fall, or heat resistance worsens, or, Since a molecular weight of poly imide siloxane obtained becomes low, solubility over an organic solvent falls or compatibility with other organic compounds worsens, a thing of said extent is suitable.

[0016]As an example of a diaminopolysiloxane shown by a general formula (1), omega, and omega'- bis(2-aminoethyl)poly dimethylsiloxane, omega, omega'-bis(3-aminopropyl)poly dimethylsiloxane, An omega and omega'-bis(4-aminophenyl)poly dimethylsiloxane, omega, and omega'- bis(4-amino-3-methylphenyl)poly dimethylsiloxane, omega, omega'-bis(3-aminopropyl)polydiphenyl siloxane etc. can be mentioned suitably.

[0017]As aromatic diamine used with a diaminopolysiloxane, An aromatic diamine compound which, especially generally, has two or more aromatic rings [2-5], such as the benzene ring, For example, a biphenyl system diamine compound, a diphenyl ether system diamine compound, A benzophenone series diamine compound, a diphenylsulfone system diamine compound, A diphenylmethane system diamine compound, a diphenyl propane system diamine compound, A 2,2-bis(phenyl)hexafluoropropane system diamine compound, A diphenylene sulfone system diamine compound, a JI (phenoxy) benzenoid diamine compound, A JI (phenyl) benzenoid diamine compound, a bis(phenoxyphenyl)sulfone series diamine compound, A bis(phenoxyphenyl)hexafluoropropane system diamine compound, a bis (phenoxyphenyl)propane system diamine compound, etc. can be mentioned, and they can be used as independence or a mixture.

[0018]As an example of aromatic diamine, 1,4-diaminodiphenyl ether, Diphenyl ether system diamine compounds, such as 1,3-diaminodiphenyl ether, JI (phenoxy) benzenoid diamine compounds, such as 1,3-JI (4-diaminophenoxy) benzene and 1,4-bis(4-aminophenoxy) benzene, 2,2-bis[4-(4-aminophenoxy) phenyl] propane, Bis(phenoxyphenyl)propane system diamine compounds, such as 2,2-bis[4-(3-aminophenoxy) phenyl] propane, ********** which has 2-5 aromatic rings, such as JI (phenoxyphenyl) sulfone system diamine compounds, such as bis[4-(4-aminophenoxy) phenyl] sulfone and bis[4-(3-aminophenoxy) phenyl] sulfone, can be mentioned suitably.

[0019]in this invention -- a diaminopolysiloxane and aromatic diamine -- the former -- 10-80-mol % -- desirable -- 15-70-mol % -- further -- desirable -- 20-60-mol % and the latter -- 20-90-mol % -- desirable -- 30-85-mol % -- it is used at 40-80-mol% of a rate still more preferably. Since there are too many one of ingredients, or solubility over an organic solvent of poly imide siloxane will fall if it is too few and separates from these ranges, or compatibility with other

organic compounds worsens or an elastic modulus becomes high, it is not suitable.
[0020]In this invention, poly imide siloxane (a) is manufactured by a following method.
(a_1) Abbreviation equimolar use of the diamine component of an aromatic tetracarboxylic acid ingredient, a diaminopolysiloxane, and aromatic diamine is carried out, and they are a polymerization and a method of making it imide-ize and obtaining poly imide siloxane at temperature of 15-250 ** continuously in an organic polar solvent.
[0021](a_2) dividing a diamine component -- first -- an excessive amount of an aromatic tetracarboxylic acid ingredient, and a diaminopolysiloxane -- the inside of an organic polar solvent -- temperature of 15-250 ** -- a polymerization -- and it being made to imide-ize and, An imide siloxane oligomer which has acid or an acid anhydride group is adjusted to a with an average degree of polymerization of about one to ten end, An aromatic tetracarboxylic acid ingredient and an excessive amount of aromatic diamine are independently polymerized at temperature of 15-250 ** in an organic polar solvent, Imide-izing and an imide oligomer which makes it imide-ize and has an amino group at the with an average degree of polymerization of about one to ten end are adjusted, Subsequently, a method of mixing these both so that an acid component and a diamine component may become abbreviation equimolar, making it react at temperature of 15-60 **, and also carrying out temperature up of the temperature to 130-250 **, and obtaining poly imide siloxane of a block type.
[0022](a_3) Abbreviation equimolar use of an aromatic tetracarboxylic acid ingredient, a diaminopolysiloxane, and the aromatic diamine component is carried out, and once making it polymerize at temperature of 20-80 ** first in an organic polar solvent and obtaining polyamic acid, a method of imide-izing and obtaining poly imide siloxane, etc. are.
[0023]As an organic polar solvent used for manufacture of poly imide siloxane by this invention, For example, N,N-dimethylacetamide, a N,N-diethylacetamide, Amide system solvents, such as N.N-dimethylformamide, a N,N-diethylformamide, and N-methyl-2-pyrrolidone, Dimethyl sulfoxide, diethyl sulfoxide, a dimethylsulfone, A solvent containing sulfur atoms, such as diethyl sulfone and hexamethyl sulfo RUAMIDO, A solvent of others which have oxygen atoms, such as phenol system solvents, such as cresol, phenol, and a xylenol, acetone, methanol, ethanol, ethylene glycol, dioxane, and a tetrahydrofuran, in intramolecular, such as a solvent, pyridine, and tetramethylurea, can be mentioned. If required, it is also possible to use together an organic solvent of other kinds like aromatic hydrocarbon system solvents, such as benzene, toluene, and xylene, solvent naphtha, and benzonitrile.
[0024]Although poly imide siloxane may use what was obtained by which methods, such as aforementioned (a_1) - (a_3), in this invention, an imidization ratio is high in the amount of polymers as much as possible, and adhesives with adhesion operation and adhesion performance which what can be especially boiled and dissolved in an organic polar solvent at

least 3% of the weight or more at about 5 to 40% of the weight of high concentration is sufficient are preferred at that of ******.

[0025]Measure an imidization ratio of poly imide siloxane with an infrared-absorption-spectrum analysis method, and an imidization ratio Not less than 90%, It is preferred that it is the high imidization ratio that especially not less than 95% is preferred, and an absorption peak concerning an amic acid linkage of polymer is not substantially found out in infrared-absorption-spectrum analysis, but only an absorption peak concerning imide ring combination is seen.

[0026]Logarithmic viscosity (density measurement: a 0.5g [/100 ml] solvent, solvent:N-methyl-2-pyrrolidone, measurement temperature:30 **, viscosity meter:canon Fenske type viscosity meter) of poly imide siloxane is 0.05-4, and a polymer that is 0.1 to about three still more preferably.

[0027]When the aforementioned poly imide siloxane is formed in a film, The elastic modulus of below 250kg[/mm] ^{2} is 0.5-200kg[/mm] ^{2} especially, not less than 250 ** of pyrolysis starting temperature is especially not less than 300 ** -- secondary transition temperature -not less than 10 **, when that it is about 10-250 ** attains the purpose of this invention, it is especially preferred.

[0028]The amount of epoxy polyoxyalkylene modified polysiloxane (b) used used in this invention is 1.5 - 15 weight section preferably one to 60 weight section to poly imide siloxane 100 weight section. there is not too much amount used, or if too small, compatibility with other ingredients will worsen and it will not become a uniform solution, or an effect shows up -- since it becomes, said range is suitable.

[0029]As epoxy polyoxyalkylene modified polysiloxane used in this invention, Reactant polysiloxane oil which has a hydroxyl group, a carboxyl group, or an amino group at the end, Bisphenol type epoxy resin, phenol novolak type epoxy resin, An epoxy compound and polyoxypropylene, such as a glycidyl ether type epoxy resin and glycidyl ester typed epoxy resin, . Are obtained by making polyoxyalkylene compounds, such as a polyoxyethylene, react at temperature of about 80-140 **. What is necessary is just epoxy polyoxyalkylene modified polysiloxane which has at least one epoxy group an end or inside a polysiloxane, and also has at least one for a polyoxyalkylene group.

[0030]As epoxy polyoxyalkylene modified polysiloxane, a thing whose melting point is 90 ** or less, or a thing which is 30 ** or less is preferred. It is preferred that it is what an epoxy polyoxyalkylene denaturation siloxane has at least one epoxy group, and also has at least one polyoxyalkylene group. For example, an epoxy polyoxyalkylene denaturation silicone oil (Dow Corning Toray Silicone [, Inc.] make: SF-8421EG and BY-16-845, BY-16-876 grade) can be mentioned.

[0031]A using rate of other epoxy compounds (c) which have an epoxy group used in this

invention, To poly imide siloxane 100 weight section, if it is 20 to 150 weight section preferably and is too small in many [too] 15 to 250 weight section, Since adhesives of an uncured state are sticky, pliability after hardening is missing, or softening temperature of adhesives of an uncured state is too high and the adhesion characteristic after hardening worsens, it is desirable to use said range.

[0032]As other epoxy compounds which are used in this invention and have an epoxy group, an epoxy compound which has one or more epoxy groups, for example, a bisphenol A type, and bisphenol F type epoxy resin (oil recovery shell incorporated company make.) Trade name : Epicoat 807, 828 grades, phenol novolak type epoxy resin, An alkyl polyhydric phenol type epoxy resin (the Nippon Kayaku make, RE701, RE550S grade), A polyfunctional mold epoxy resin (the Sumitomo Chemical Co., Ltd. make, ELM-100 grade), A glycidyl ether type epoxy resin, glycidyl ester typed epoxy resin, glycidyl amine type epoxy resin (the Mitsubishi Gas Chemical [Co., Inc.] make, a trade name: Thet Ladd X grade), etc. are independent, or can also use more than one together. Since softening temperature of adhesives of an uncured state will become high if the melting point of an epoxy compound is too high, what has the melting point especially liquefied at a thing which is about 0-80 **, or temperature of 30 ** or less 90 ** or less is preferred.

[0033]As an inorganic bulking agent (d) used in this invention, primary particle diameter can mention preferably 2 micrometers or less of silicon oxide, oxidation aluminum, titanium oxide, etc. which are 1 micrometer or less still more preferably. [5 micrometers or less of] For example, silicon oxide made from Japanese Aerosil, Inc. (trade name: Aerosil 200, Aerosil 300, Aerosil R202, Aerosil R972 grade), Silicon oxide by Shionogi& Co., Ltd. (trade name: Carplex 80 grade), silicon oxide by Cabot Corp. (trade name: KYABO seal TS-720 grade), etc. can be mentioned.

[0034]A using rate of an inorganic bulking agent used in this invention, Since being 0.6 to 15 weight section preferably 0.2 to 20 weight section, and it being too few, or it being ineffective if too large, or adding uniformly, and churning and mixing become difficult to poly imide siloxane 100 weight section, said range is preferred.

[0035]As an epoxy curing agent (e) used in this invention, Curing catalysts, such as a hardening agent publicly known in itself, for example, imidazole derivatives, tertiary amine, and triphenylphosphines, Polyaddition mold-curing agents, such as a phenol novolac mold-curing agent which has dicyandiamides, type hydrogen, aromatic diamine, and a hydroxyl group, organic peroxide, etc. can be mentioned.

[0036]Generally the amount of epoxy curing agent used is. 0.01-110 weight-section use is carried out to epoxy compound 100 weight section.

[0037]Heat-resistant adhesives of this invention The aforementioned poly imide siloxane (a) epoxy polyoxyalkylene modified polysiloxane (b), Uniformly, it can agitate and mix and the

specified quantity of an epoxy compound (c) of others which have an epoxy group, an inorganic bulking agent (d), and an epoxy curing agent (e) can be obtained easily. When mixing, after an ultrasonic wave etc. may be used and making it distribute in a suitable polar solvent beforehand so that it may not condense selectively, it can mix with other ingredients of adhesives, and said inorganic bulking agent can be used as a solution composition of heat-resistant adhesives. Amide series solvents, such as a solvent, N-methyl-2-pyrrolidone, etc. which have in intramolecular oxygen atoms, such as an organic polar solvent which can be used as an organic polar solvent when obtaining said poly imide siloxane, for example, dioxane, and a tetrahydrofuran, are used suitably.

[0038]5 to 40 % of the weight is preferably suitable for concentration of a solution composition three to 50% of the weight, and, as for solution viscosity (30 **), it is still more preferably [especially] preferred that it is about 0.3-1000 poise 0.2-5000 poise 0.1-10000 poise.

[0039]As for heat-resistant adhesives of this invention, it is preferred that 150 ** or less of softening temperature [140 ** or less of] (temperature which softening starts on a hot platen) of a constituent of only an unhardened resinous principle is about 0-130 ** still more preferably especially.

[0040]Heat-resistant adhesives of this invention a solution composition of heat-resistant adhesives by which all the above-mentioned resinous principles are dissolved in an organic polar solvent, Heat-resistant film planes, such as a suitable metallic foil, an aromatic polyimide film, and aromatic polyester, Or by applying on a film plane of thermoplastics, such as polyethylene, and drying the coating layer for [20 seconds -] 100 minutes at temperature of 80-200 **, A thin film (about 1-200 micrometers in thickness) of heat-resistant adhesives of an uncured state (a solvent survival rate is 0.5 or less % of the weight preferably) from which a solvent was substantially removed to 1 or less % of the weight can be formed.

[0041]A thin film of heat-resistant adhesives which are not hardened [which was manufactured as mentioned above] has suitable pliability, and twists it around a paper tube etc., or, Or a lamination layer sheet which can also carry out perforating processes, such as a punching method, and in which a thin film layer of unhardened heat-resistant adhesives is formed on the further aforementioned heat resistance or a thermoplastic film, It is also possible to transfer a sheet layer of heat-resistant adhesives on a metallic foil for transfer places or a heat-resistant film by piling up a metallic foil or a heat-resistant film for transfer places, etc., and letting between rolls (laminate roller) of a couple heated by temperature of about 20-200 ** pass.

[0042]In order to join a metallic foil etc. to a heat-resistant film using heat-resistant adhesives of this invention and to form layered products, such as a copper-clad board, For example, especially a heat-resistant film and a metallic foil 80-200 ** via a filmy heat-resistant adhesives layer formed as mentioned above at temperature of 120-180 **. Laminate under application of pressure (0.2-8kg[/cm] ^{2}) (lamination), and further the laminated thing especially about 140-

250 ** at temperature of 150-230 **. By heating for 1 to 30 hours and carrying out heat cure of the heat-resistant adhesives layer especially, for for 30 minutes to 40 hours, there is also no trouble and a layered product can be manufactured continuously easily.

[0043]Heat-resistant adhesives of this invention can be conveniently used, in order to join to heat-resistant films, such as an aromatic polyimide film, a polyamide film, a polyether ether ketone film, and a polyether sulfon film, and suitable metallic foils, such as copper, aluminum, and iron. Other thermosetting resin, such as a bismaleimide resin, may contain heat-resistant adhesives of this invention at few rate as a resinous principle.

[0044]If heat-resistant adhesives of this invention are used and a section of a glue line after adhesion / hardening is observed with a transmission electron microscope (drawing 1), it will distribute as particles which became independent in matrix resin of an adhesives layer, moreover a particulate material with a particle diameter of 0.1-5 micrometers will be formed, and it will be observed that an adhesives layer has sea island structure. Since an adhesion side will become uneven if particle diameter of a particulate material becomes larger than 5 micrometers, intensity of an adhesives layer becomes weak and is not preferred. Adhesion - Since inorganic bulking agents which such sea island structure was taken after hardening, and were added have gathered for an island portion, it has heat resistance and the characteristic excellent in balance of pliability, and it contributes also to adhesive stability. Such a gestalt tends to make destructive mode cohesive failure in a friction test, and, as for it, adhesive strength is stabilized.

[0045]

[Example]Hereafter, an example is shown and this invention is explained in more detail. In the following examples, logarithmic viscosity (eta_{inh}), It is the value which dissolved poly imide siloxane in N-methyl-2-pyrrolidone uniformly, prepared the solution, measured the solution viscosity of the solution, and the viscosity of ****** at 30 ** using the canon Fenske type viscosity meter, and was computed from the following formula so that concentration may serve as a 0.5g/100ml solvent.

[0046]

[Formula 1]

$$\text{対数粘度}\ (\eta_{inh}) = \frac{\ln(\text{溶液粘度}/\text{溶媒粘度})}{\text{溶液の濃度}}$$

[0047]The softening temperature of a poly imide siloxane film is the value which asked for Tandelta (elevated-temperature side) of the viscoelasticity peak in a viscoelasticity examination using mechanical spectrometer RDS-2 by a LEO melic company.

[0048]The elastic modulus of a poly imide siloxane film is the result of measuring on condition of for 5-mm/in exfoliation speed using the tension tester by Inn Tesco, Inc.

[0049]In the process in which the workability of adhesives forms various layered products using heat-resistant adhesives, Tuck nature (adhesiveness with the film for protection), the punching nature of a layered product, and the workability at the time of a heating bond are evaluated synthetically, O shows ****, O shows good, ** is common and x shows a defect.
[0050]Adhesive strength is the result of being a part for 50-mm/in exfoliation speed, and measuring by doing a 180-degree friction test at 90 degrees and the measurement temperature of 180 ** with the measurement temperature of 25 ** using the tension tester by Inn Tesco, Inc.
[0051]Formula [curvature-radius (mm) $=L^2 / 8h$] the curvature radius which shows the curl-proof nature of the patchboard after forming a copper-clad board using heat-resistant adhesives, carrying out the etching process of the copper foil and removing it was indicated to be to JIS C5012 (L:sample length, h: height of camber) It is the value ** computed.
[0052][Manufacture of an imide siloxane oligomer]
In glass flasks with a provided with reference example 1 thermometer, brewing and a distillate mouth, and the agitator capacity of 500 ml. 0.054 mol of 2,3,3',4'-biphenyl tetracarboxylic dianhydride (a-BPDA), omega and omega'-bis(3-aminopropyl)poly dimethylsiloxane (Shin-etsu silicon incorporated company make.) Teach X-22-161AS, n:9 0.027 mol, and 160 g of N-methyl-2-pyrrolidone (NMP), raise to the temperature of 50 ** in a nitrogen air current, agitate at this temperature for 2 hours, make amic acid oligomer generate, and it ranks second, Temperature up of the reaction mixture was carried out to 200 **, and the imide siloxane oligomer (A-1 ingredient, average-degree-of-polymerization:1) which agitates at the temperature for 3 hours, and has an anhydrous group at the end was manufactured.
[0053]Used a-BPDA, the diaminopolysiloxane (X-22-161AS), and NMP of the quantity shown in the reference example 2 - the 3 1st table, respectively, and also. The imide siloxane oligomer (A-2, average-degree-of-polymerization:2 and A-3, average-degree-of-polymerization:6) which has an anhydrous group at the end like the reference example 1 was manufactured, respectively.
[0054][Manufacture of an imide oligomer]
a-BPDA of the quantity shown in the reference example 4 1st table, a 2,3,3',4'-screw [Teach 4-(4-aminophenoxy) phenyl] propane (BAPP) and NPA like the reference example 1, respectively, agitate at 50 ** among a nitrogen air current for 2 hours, make amic acid oligomer generate, and it ranks second, Temperature up of the reaction mixture was carried out to 200 **, and B-1 ingredient (average degree of polymerization: 1) of imide oligomers which agitate at the temperature for 3 hours, and have an amino group at the end were made to generate.
[0055]B-2 ingredients (average degree of polymerization: 2) of imide oligomers which a-BPDA, BAPP, and NMP which are shown in the reference example 5 - the 6 1st table were used, respectively, and also have an amino group at the end like the reference example 4, and B-3

ingredients (average degree of polymerization: 10) were manufactured, respectively.

[0056]

[Table 1]

第 1 表

参考例	酸成分	ジアミン成分		溶媒
:略号	a－BPDA (モル)	X－22－161 (モル)	BAPP (モル)	NMP (g)
1 ; A-1	0.054	0.027	———	160
2 ; A-2	0.045	0.030	———	160
3 ; A-3	0.042	0.036	———	175
4 ; B-1	0.035	———	0.070	155
5 ; B-2	0.044	———	0.066	160
6 ; B-3	0.055	———	0.060	165

[0057][Manufacture of poly imide siloxane]

The imide siloxane oligomer manufactured by the reference example 7 reference example 3. (A-3 ingredients) 20% of the weight of the NMP solution of 0.0025 mol of imide oligomers (B-3 ingredients) manufactured by the 0.0025-mol 20-% of the weight NMP solution and the reference example 7 is taught to glass flasks with a capacity of 500 ml, Like the reference example 1, among the nitrogen air current, temperature up was carried out and it agitated at 50 ** for 1 hour, and it was made to generate, and it ranked second, temperature up of the polyamic acid block polymer was carried out, it agitated at 200 ** for 3 hours, and poly imide siloxane (block polymer) was made to generate. This poly imide siloxane is not less than 95% in imidization ratio.

Logarithmic viscosity was 0.45.

[0058]It was used by quantity and a reaction condition as show each oligomer manufactured by the reference example 8 - the reference examples 1-6 of 9 above-mentioned in the 2nd table, and also poly imide siloxane (block polymer) was manufactured like the reference example 7, respectively. The elastic modulus and softening temperature at the time of molding into the logarithmic viscosity of each manufactured poly imide siloxane and a film are shown in the 2nd table.

[0059]

[Table 2]

第 2 表

参考例	A 成分 種類	A 成分 使用量 (モル)	B 成分 種類	B 成分 使用量 (モル)	ポリイミドシロキサン溶液 ポリマーの対数粘度	ポリイミドシロキサン溶液 シロキサン単位の含有率 (モル%)	ポリイミドシロキサンフィルム 厚み (μm)	ポリイミドシロキサンフィルム 弾性率 (kg/mm²)	ポリイミドシロキサンフィルム 軟化温度 (℃)
7	A−3	0．0025	B−3	0．0025	0．45	33．33	25	35	160
8	A−1	0．0150	B−1	0．0150	0．46	33．33	25	70	170
9	A−2	0．0100	B−2	0．0100	0．48	40．00	25	60	185

注）ポリマー中のシロキサン単位含有率＝（ジアミノシロキサン使用量／全ジアミン化合物使用量）×100（モル%）

[0060]Example 1 [Preparation of the solution composition of heat-resistant adhesives] 50 g of poly imide siloxane (block polymer, A-3-B-3), epoxy polyoxyalkylene modified polysiloxane

which were manufactured by the aforementioned reference example 7 by glass flasks with a capacity of 500 ml [The product made from Toray Industries Dow KONIN Silicone, SF-8421EG] 10 g, an epoxy resin [The product made from Oil recovery Shell Epoxy, Epicoat 807] 30 g, silicon oxide [Japanese Aerosil, Inc., Aerosil 200, particle diameter:0.012micrometer] 3.0 g, the phenol novolac mold-curing agent (made in Meiwa Chemicals, Inc., H-1) 20g and the imidazole series hardening agent 0.1g, and the dioxane 185g were prepared, it agitated at the room temperature (25 **) for about 2 hours, and the solution composition (viscosity of 25 **: 7 poise) of uniform heat-resistant adhesives was prepared. Even if it neglected this solution composition for one week to the room temperature, it held the state of the uniform solution.
[0061][Manufacture of the layered product by heat-resistant adhesives] Apply the solution composition of the above-mentioned heat-resistant adhesives by a thickness of 125 micrometers with a doctor blade on a polyimide film (the Ube Industries, Ltd. make, trade name:UPILEX-S, and 75 micrometers in thickness), and it ranks second, The coating layer was heated for 30 minutes at 100 ** for 30 minutes at 50 **, it dried, and the heat-resistant adhesives layer (a layer, softening temperature by which un-hardening was dried: 60 **) about 25 micrometers thick was formed on the polyimide film.
[0062]The polyimide film which has this heat-resistant adhesives layer, and the smooth field (field which has not carried out roughening treatment) of copper foil (35 micrometers) are piled up, It was stuck by pressure by making it pass, applying a pressure between the laminate rollers heated at 130 **, and it heat-treated at 100 ** for 1 hour, this layered product stuck by pressure was heat-treated at 160 ** at 120 ** for 10 hours for 1 hour, the heat-resistant adhesives layer was stiffened, and the layered product was manufactured. Adhesive strength is measured about the obtained layered product, and the result is shown in the 3rd table.
[0063]Use the poly imide siloxane (block polymer) manufactured by each reference examples 8-9 as shown in Example 2 - the 4 3rd table, and the presentation of each ingredient was shown in the 3rd table, and also the solution composition of heat-resistant adhesives was prepared like Example 1, respectively. Each aforementioned solution composition was used, and also the layered product was manufactured like Example 1, respectively. The performance of the layered product is shown in the 3rd table, and an electron microscope photograph is shown in drawing 1 (x9000). Any example was the same as that of drawing 1.
[0064]
[Table 3]

第３表

例		耐熱性接着剤の溶液組成物										接着剤層	積層体	
	参考例	ポリイミドシロキサン 特数粘度 η_{inh}	ポリシロキサン 単位（モル数）	量（g）	エポキシ変性ポリシロキサン 種類	量（g）	他のエポキシ化合物 種類	量（g）	無機充填剤 種類	量（g）	エポキシ硬化剤 種類	量（g）	溶媒 量（g）	30℃でのゼラチン化性	接着剤層の接着性（kg/cm）25℃ 180℃	エッチングファイルムの曲率半径（mm）
実施例	1	0.45	33.33	50	SP-8421EG	10	エピコート807	30	アエロジル200	8	H-1	20	185	◎	1.8 0.7	110
	2	0.46	33.33	50	BY-16-845	10	エピコート807 RESOUS	20 5	アエロジル200	6	H-5	15	185	○	1.9 0.8	120
	3	0.46	33.33	50	BY-16-875	5	エピコート807 RESOUS	20 6	キャボシールTS-720	2	H-5	19	185	◎	1.8 0.8	100
	4	0.48	40.00	50	SP-8421EG	5	エピコート807 EXA-100	16 6	キャボシールTS-720	3	H-1 H-5	15 2	185	◎	1.9 0.8	120
比較例	1	0.45	33.33	50	SP-8421EG	10	エピコート807	30	——	—	H-1	20	185	○	0.7 0.3	110

エポキシ硬化剤：イミダゾール系硬化剤 0.1g 含有。粒子径（μm）：アエロジル200:0.012，キャボシールTS-720:0.02。溶媒：ジオキサン。

[0065]Comparative example 1 inorganic bulking agent was not used, and also the solution composition of heat-resistant adhesives was adjusted like Example 1. The solution composition was used, and also said solution composition was applied on the polyimide film

like Example 1, it dried, and the adhesives layer (an adhesives layer, thickness by which un-hardening was dried: 20 micrometers) was formed.
[0066]The polyimide film which has the aforementioned adhesives layer was used, and also the layered product was manufactured like Example 1. Although the result of the system performance testing of the layered product was shown in the 3rd table, the adhesive property was as low as 0.7 kg/cm.
[0067]In the column of "the kind of epoxy polyoxyalkylene modified polysiloxane" of the 3rd table, "SF-8421EG", "BY-16-845", and "BY-16-876", Epoxy Dow Corning Toray Silicone polyoxyalkylene modified polysiloxane is shown. the 3rd table -- "-- others -- in the column of kind" of an epoxy compound, "Epicoat 807" the bisphenol A type epoxy resin made from Oil recovery Shell, [show and] "RE701" and "RE550S" show the alkyl polyhydric phenol type epoxy resin by Nippon Kayaku Co., Ltd., and "ELM-100" shows the polyfunctional mold epoxy resin by Sumitomo Chemical Co., Ltd.
[0068]
[Effect of the Invention]By applying that solution composition on a support film, and drying at low temperature comparatively, the heat-resistant adhesives of this invention can form easily the heat-resistant adhesives layer of a thin layer state by un-hardening, and, moreover, have pliability with a sufficient adhesives layer made from a heatproof of that thin layer.
and it being also possible for it to be convenient in any way, even if the heat-resistant adhesives layer of the thin layer on the support film receives a perforating process, and to transfer at a suitable temperature to up to the support film of other heat resistance, and, The workability which can carry out comparatively a lamination with a heat-resistant film and copper foil at low temperature is good.

[0070]The heat-resistant adhesives of this invention show adhesive strength also with a high layered product with a smooth metallic foil, and also after heat cure is carried out, they are excellent in heat resistance, flexibility, etc.
And since curl of the etching film after etching of copper foil etc. is also small, it can be especially used conveniently as adhesives, such as a flexible wiring board and a copper-clad board for TAB.

[Translation done.]